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14. ABSTRACT

A high modulus, sulfonated ionomer synthesized from 4,6-bis(4-hydroxyphenyl)-N,N-diphenyl-1,3,5-triazin-2-amine and 4,40-biphenol with bis(4-fluorophenyl)sulfone (DPA-PS:BP) is investigated for ionic polymer actuators. The uniqueness of DPA-PS:BP is that it can have a high ionic liquid (IL) uptake and consequently generates a high intrinsic strain response, which is >1.1% under 1.6 V while maintaining a high elastic modulus (i.e. 600 MPa for 65 vol% IL uptake). Moreover, such a high modulus of the active ionomer, originating from the

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A highly aromatic and sulfonated ionomer for high elastic modulus ionic polymer membrane micro-actuators

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Abstract
A high modulus, sulfonated ionomer synthesized from 4,6-bis(4-hydroxyphenyl)-*N*,*N*-diphenyl-1,3,5-triazin-2-amine and 4,4′-biphenol with bis(4-fluorophenyl)sulfone (DPA-PS:BP) is investigated for ionic polymer actuators. The uniqueness of DPA-PS:BP is that it can have a high ionic liquid (IL) uptake and consequently generates a high intrinsic strain response, which is $>1.1\%$ under 1.6 V while maintaining a high elastic modulus (i.e. 600 MPa for 65 vol% IL uptake). Moreover, such a high modulus of the active ionomer, originating from the highly aromatic backbone and side-chain-free structure, allows for the fabrication of free-standing thin film micro-actuators (down to 5 μm thickness) via the solution cast method and focused-ion-beam milling, which exhibits a much higher bending actuation, i.e. 43 μm tip displacement and 180 kPa blocking stress for a 200 μm long and 5 μm thick cantilever actuator, compared with the ionic actuators based on traditional ionomers such as Nafion, which has a much lower elastic modulus (50 MPa) and actuation strain.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Ionic metal polymer composites (IPMCs) are a class of ionic electro-active polymers (i-EAPs) in which the drifting and diffusion of mobile ions under an applied voltage cause accumulation or depletion of excess ions at the electrodes, resulting in an expansion or contraction in these regions, thus generating bending actuation as illustrated in figure 1. The IPMC actuators are attractive because large actuations can be generated under low applied voltages ($\sim$a few volts) [1–3], which makes them very attractive for many electromechanical transduction applications such as polymer-based microelectromechanical systems (p-MEMS), artificial muscles, biomimetic actuators, soft robotic actuation and energy harvesting [4–14]. Illustrated in figure 1 is the basic structure of IPMC actuators, consisting of an electrolyte-containing polymer membrane sandwiched between two electrodes. In many IPMC actuators investigated, nanoporous electrodes are employed to increase the electrode surface area [1–5].

In order to generate high electromechanical responses, i-EAPs such as IPMCs should contain a high volume content of electrolytes to boost the mobile ion concentration and to improve the ion mobility. However, one severe drawback of absorbing high volume content electrolytes in the traditional ionomers used in IMPCs such as Nafion^{TM} and Aquivion^{TM} membranes is the drastic reduction of the elastic modulus of the ionomer. Since the blocking force is

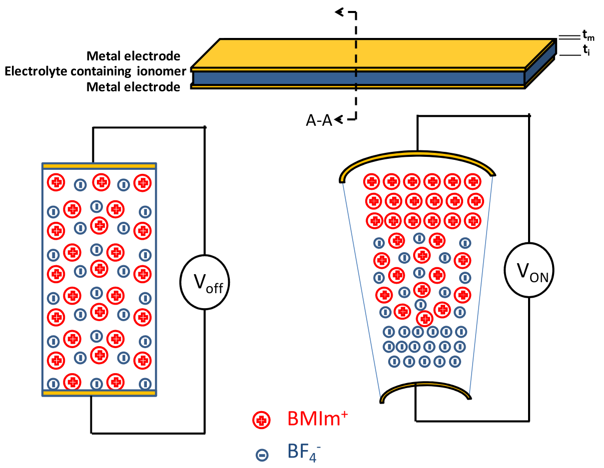

Figure 1. Schematics of an ionic membrane actuator where t_m and t_i are the thicknesses of the metal electrode and ionomer membrane, respectively. In this study, DPA-PS:BP is used as the ionomer and 1-methyl-3-butylimidazolium tetrafluoroborate ([BMIm][BF_4]) is used as the electrolyte. The ion transport and storage at the electrodes (cross section A–A) causes a bending actuation when a voltage is applied to metal electrodes of the membrane actuator.

proportional to the Young's modulus of the actuator, this reduction greatly lowers the blocking force, which is a key actuator performance parameter [15–18]. The low modulus also causes thin Nafion^{TM} or Aquivion^{TM} membranes losing robustness, thus preventing them from being effectively employed in MEMS applications.

Herein, an in-house synthesized highly aromatic sulfonated poly(arylene ether sulfone)s with 1,3,5-s-triazin ionomer, DPA-PS:BP (1:1), is introduced as a new ionomer membrane for the i-EAP actuators which has the capability of swelling high volume fraction (∼64 vol% or 150 wt%) of ionic liquids (ILs) to generate a high strain while maintaining a high elastic modulus (∼0.6 GPa). Moreover, the high elastic modulus of the IL-containing ionomer membrane allows the fabrication of micro-actuators of 5 μm thick via solution casting. The as-made micro-actuators exhibit a large bending actuation, a high blocking force and no back relaxation. This is in great contrast to the i-EAPs with Nafion^{TM} and Aquivion^{TM} ionomer membranes, which have severe back relaxations, i.e. the actuators bend initially towards one direction and then relax back to bend towards the opposite direction [13, 19, 20].

2. Experimental details

DPA-PS:BP was synthesized by polycondensation reaction of 4,6-bis(4-hydroxyphenyl)-*N*,*N*-diphenyl-1,3,5-triazin-2-amine and 4,4′-biphenol with bis(4-fluorophenyl)sulfone in one-to-one ratio. Details of the polymer synthesis and the polymer's properties have been described earlier [21, 22]. Figure 2(a) presents the chemical structure of the highly aromatic DPA-PS:BP, where the polymer backbone consists of benzene rings interconnected with either oxygen or sulfone groups and a 1,3,5-s-triazine ring. The actuation of IPMCs is based on the transport of ions through the polymer matrix and the accumulation or depletion of excess ions at two electrodes when subject to an applied voltage. The mobile ions are contributed by the electrolytes, for example, cations and anions in ILs. In this study, an imidazolium based room temperature IL, 1-methyl-3-butylimidazolium tetrafluoroborate ([BMIm][BF_4]), which was previously used in IPMC actuators, is utilized as the electrolyte [15]. The chemical structure of [BMIm][BF_4] is presented in figure 2(b) and, as can be seen, $BMIm^-$ and BF_4^+ show a large ion size difference (3.2/1 molecular volume ratio) [15].

Thin DPA-PS:BP membranes with different IL uptakes were prepared using a solution cast method. DPA-PS:BP powder was dissolved in *N*-methyl-2-pyrrolidone (NMP) at 80 °C and stirred for 24 h until the powder was completely dissolved. Afterwards, [BMIm][BF_4] was added to the solution in desired weight percentages. The solution was

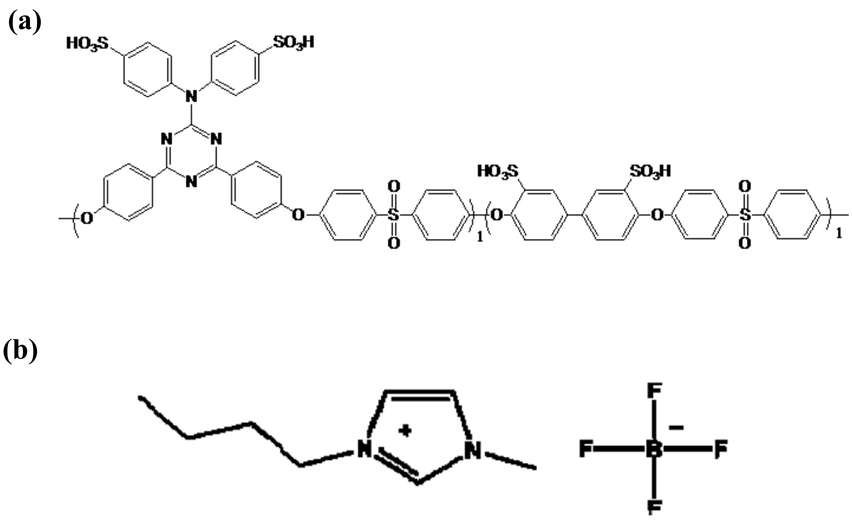

Figure 2. The chemical structures of (a) DPA-PS:BP and (b) [BMIm][BF_4].

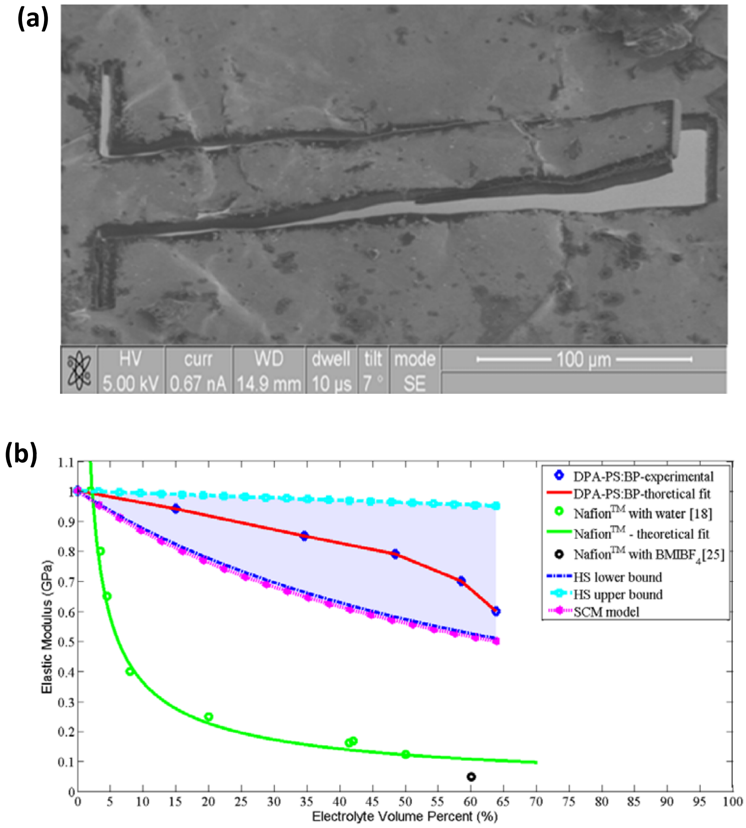

Figure 3. (a) TEM image of the micro-actuator fabricated. (b) The elastic modulus of DPA-PS:BP as a function of $[BMIm][BF_4]$ uptake. The elastic modulus of Nafion™ 117 as a function of water uptake from [18] and Nafion™ 211 with ∼60 vol% (40 wt%) of $[BMIm][BF_4]$ uptake is also presented as a comparison [25].

Table 1. The FIB parameters for deposition-free cutting.

FIB milling parameters	
Ion beam current (nA)	7
Dwell time (μs)	2.4
Volumetric removal (μ^3 min^{-1})	86.6
Total cutting time (min)	50

further sonicated for more than 5 h and was then cast on silicon wafers and dried for 20 h at 80 °C. Due to its high elastic modulus, as thin as 5 μm thick free-standing films with high IL uptake (and hence high ionic conductivity) were fabricated. It is noted that, in several earlier studies, the electrolytes were introduced into the polymer matrix by soaking it directly in electrolytes. However, for DPA-PS:BP films, the soaking method does not allow for high IL uptake in the films (<1 wt%).

To demonstrate an IL-containing thin film DPA-PS:BP micro-actuator, a 200 μm × 33 μm micro-cantilever of 5 μm thick was fabricated by employing the focused-ion-beam (FIB) milling. It is a great challenge to manufacture microstructures out of ionic polymer membranes containing IL by using lithography and other wet chemical or dry etching techniques. For example, IL tends to be released from the polymer matrix when the IL-containing membrane is dipped into another solution in lithography and other wet chemical techniques for MEMS fabrication. Here, a top-down approach like FIB is preferred over traditional MEMS manufacturing techniques of using lithography and other wet chemical techniques [23].

The FIB milling parameters are material-dependent [24]. For this polymer, the re-deposition due to the high momentum impact of Ga^+ ions was a major problem during milling. Despite being milled quickly, the milling parameters had to be carefully tuned to obtain a cleanly cut cantilever structure. The parameters used during the milling of this structure are listed in table 1. This method also allows the design and fabrication of micro-actuators with different shapes for various application purposes. For the electromechanical characterization, the micro-actuator is excited by applying an incremental step voltage. The SEM micrograph of the micro-actuator fabricated via FIB is shown in figure 3(a).

The elastic modulus of the films containing different IL uptakes was characterized by an Instron machine. Au foils of 50 nm thick were hot-pressed to the two surfaces of the membrane for electric characterization (figure 1). Planar electrodes allow for an easier micro-actuator fabrication process and offer a configuration for material property analysis. The electric impedance of the membranes with different IL uptakes was characterized by a potentiostat (Princeton 2237).

Table 2. Properties of ionomers and IL for model calculation and for comparison.

	Density (dry) (g cm^{-3})	Elastic modulus (dry) (GPa)	Bulk modulus (GPa)	Proton conductivity (S cm^{-1})	Ionic exchange capacity (mmol g^{-1})
Nafion^{TM} 117 (Cs^+)	2.06[b]	1.47[b]	16.3	1.1×10^{-2} [c]	0.86[c]
DPA-PS:BP	1.42	1.0	6.66	5.9×10^{-2} [c]	2.11[c]
[BMIm][BF_4]	1.21	—	2.6[a]	—	—

[a] The bulk modulus of [BMIm][BF_4] is calculated from isothermal compressibility values at room temperature and at 1 atm pressure from Tekin *et al* [32].

[b] Nafion^{TM} 117 density and elastic modulus values are adapted from Nemat-Nasser [18].

[c] Proton conductivity and ionic exchange of DPA-PS:BP and Nafion^{TM} 117 at room temperature are adapted from [22] and [33], respectively.

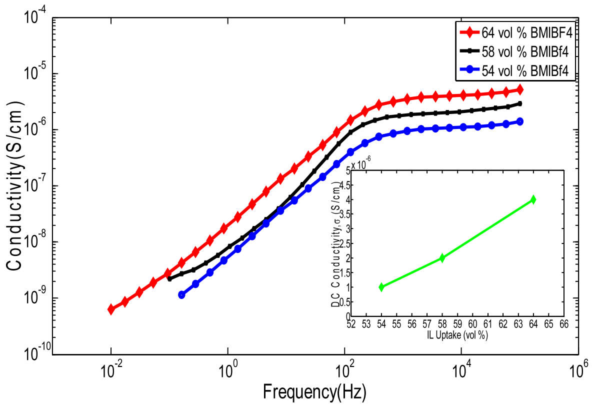

Figure 4. The conductivity versus frequency of DPA-PS:BP membrane with different IL uptakes. Inset shows the intrinsic ionic conductivity of the membrane vs IL uptake (from 54 vol% to 64 vol%).

3. Results and discussions

Presented in figure 3(b) is the elastic moduli of the DPA-PS:BP films as a function of the electrolyte volume per cent (vol%). The elastic modulus (Y) of DPA-PS:BP shows a slow and nearly linear decrease with [BMIm][BF_4] uptake until 50 vol% uptake. Beyond that, Y exhibits a fast decrease with IL uptake. Hence, no experimental study was made beyond 64 vol% of IL uptake, at which the actuator exhibits a large bending actuation. It is noted that, even with 64 vol% IL uptake, the elastic modulus of the membrane can still maintain at a high value of 600 MPa.

In contrast, hydrated Nafion^{TM} 117, which are used widely in traditional IPMC actuators, displays a dramatic decrease of elastic moduli with electrolyte uptake [3, 18, 26, 27]. Despite the fact that the dry films of Nafion^{TM} 117 possess higher elastic modulus (1.47 GPa) than DPA-PS:BP (1 GPa), the elastic modulus of Nafion^{TM} shows a drastic decrease with IL or water uptakes as shown in figure 3(b) [18]. For example, the elastic modulus of Nafion with 60 vol% (40 wt%) of IL such as [BMIm][BF_4], which is above the critical uptake of ILs in the Nafion membrane in order to generate substantial actuation in IPMCs, is 50 MPa [25]. Such a large reduction of elastic modulus in Nafion^{TM}, which dramatically decreases the stress level of the IPMC actuators, may vary slightly for different counter ions and water uptake, but even at the 5% hydration level, the reduction of the elastic modulus is about 60%, as illustrated in figure 3(b). On the other hand, the reduction of the elastic modulus of DPA-PS:BP with 65 vol% IL uptake is only about 45%.

The higher elastic modulus of DPA-PS:BP with higher electrolyte uptake compared with traditional ionomers is due to the tailored aromatic structure of DPA-PS:BP [21]. The highly aromatic backbone provides high modulus, high glass transition temperature (>200 °C) and high thermal stability, compared with the commonly used commercial ionomers in IPMCs such as Nafion^{TM} and Aquivion^{TM} which have Teflon backbones [19]. Also, the addition of pendant diphenylamine groups increases the glass transition temperature by >50 °C over similar polymers without pendant groups [22]. As a result, DPA-PS:BP with side-chain free highly aromatic polymer structure demonstrates a more rigid and robust system while allowing a high uptake of electrolytes.

The high elastic modulus of the membrane with ILs may be understood from the model of the IL–ionomer composite consisting of spherical inclusions of IL [BMIm][BF_4] in the polymer matrix DPA-PS:BP. The experimental results are compared with the HS (Hashin–Shtrikman) model and the SCM (self-consistent method) model [28, 29]. Using the bulk modulus for [BMIm][BF_4] and the elastic modulus of DPA-PS:BP from table 2, the HS bounds and the SCM model are obtained and shown in figure 3(b). The SCM model result is identical to the HS lower bound, for which [BMIm][BF_4] is considered as an inviscid fluid [30]. The measured moduli values are bound by the HS model (shaded area) and the SCM model. At below 50 vol% IL uptake, the elastic modulus decreases with IL almost linearly. The faster and nonlinear decrease after 50 vol% uptake may be explained by the change in the IL inclusion from isolated droplets to interconnected liquid networks in the ionomer matrix.

Figure 4 presents the conductivity of the films versus frequency for the membranes with three different selected IL uptakes. The conductivity plateau at high frequency corresponds to the intrinsic ionic conductivity σ_0 of the films [31]. The intrinsic conductivity σ_0 as a function of the IL uptake is presented in the inset of figure 4(b), which increases with IL uptake and reaches 4×10^{-6} S cm^{-1} at 64 vol% IL uptake. Due to a fast reduction of elastic modulus above 60 vol% IL uptake, no experimental study was conducted to beyond 64 vol% IL uptake. The electromechanical study is carried out on ionomer membranes with 64 vol% IL uptake, which possess an elastic modulus of 600 MPa and exhibit a high actuation response.

The strain response of the micro-actuator under different voltages was characterized by a Zygo profilometer and is presented in figure 5(a). The maximum tip deflection is 42 μm for a 200 μm long actuator under 1.6 V and the micro-actuator can reach the maximum bending in less than 1 s after the application of the step voltage. Moreover, the micro-actuator can maintain that position without much drift or any back relaxation. This is in sharp contrast to the IPMC actuators studied earlier using Nafion^{TM} or Aquivion^{TM} membranes, which show back relaxation after application of a step voltage and cannot be held at a fixed position under a DC voltage [19, 20].

For the i-EAP membrane actuators, the strain can be considered as generated in two ion-rich layers (active layers), where the rest of the device are merely passive layers which add mechanical load (see the schematic in figure 1). To analyze the device performance, and for comparison, we model the membrane actuator as a five-layer system, consisting of two metal electrodes, two active layers and a middle inactive layer, and assume the intrinsic strain which is the strain generated in the active layer due to excess ions without any constraints as S_{10}^{i} and the active layer thickness is t_c [25, 34]. (See figure S.2 and the derivation in the supplementary information available at stacks.iop.org/SMS/21/055015/mmedia.) The strain in the active layer of the bending actuator becomes S_1^i [35]:

$$S_1^i = s_{11}^i T_1^i + S_{10}^i \tag{1}$$

where s_{11}^i and T_1^i are the elastic compliance and stress along the ionomer film. On the other hand, the actual strain in the passive metal layers, S_1^m, can be expressed as $S_1^m = s_{11}^m T_1^m$, where s_{11}^m and T_1^m are the elastic compliance of metal and the stress along the metal layers, respectively. Considering the equilibrium conditions, which are that the total moment M and the total force F acting on the bending structure should be zero ($\int \mathrm{d}M = 0, \int \mathrm{d}F = 0$), the intrinsic strain of the active ionomer layer, S_{10}^i, that is related to the radius of curvature, R, can then be derived as [15]

$$S_{10}^i = -\left\{ Y_m \left(\frac{2}{3} t_m^3 + 2t_m \left(t_c + \frac{t_i}{2} \right)^2 + t_m^2 \, (2t_c + t_i) \right) + Y_c \left(\frac{2}{3} t_c^3 + \frac{t_c t_i^2}{2} + t_c^2 t_i \right) + Y_i \frac{t_i^3}{12} \right\} \{ R Y_c (t_i t_c + t_c^2) \}^{-1} \tag{2}$$

where t, Y and R are thickness, elastic modulus and radius of curvature, respectively. The subscripts m, i and c denote the metal, passive ionomer and charge accumulation (active) ionomer regions, respectively. The total membrane thickness t (=5 μm) = $2t_c + t_i$. Apparently, the S_{10}^i deduced will depend on t_c. For the DPA-PS:BP actuator, S_{10}^i under 1.6 V is deduced to be 1.61%, assuming t_c is 1.5 μm. If t_c is assumed to be 2.5 μm ($t_i = 0$), $S_{10}^i = 1.1\%$. A recent study on the influence of the ionomer thickness effect on the ionomer membrane actuators indicates that the active layer thickness in ionomers should be below 2 μm [34] and hence S_{10}^i in the ionomer is larger than 1.5%, and in any case it is higher than 1.1%. For actuators, the blocking stress is another key parameter and is estimated by implementing a bimorph beam model [36]:

$$T_{bl} = \frac{3tY_{cp}}{8L} S_{10}^i \tag{3}$$

where Y_{cp} is the effective Young's modulus of the three-layer structure (see figure 1). The blocking stress of the micro-ionic cantilever is deduced to be 180 kPa.

For the comparison, a membrane actuator with commercial Nafion^{TM} 211 with 40 wt% (60 vol%) of [BMIm][BF$_4$] is also fabricated and characterized. In spite of its higher ionic conductivity (1.3×10^{-4} S cm^{-1}) compared with DPA-PS:BP with 64 vol% of [BMIm][BF$_4$] (figure 4(b)), the actuation strain in the Nafion ionomer is much smaller. For a Nafion^{TM} 211 membrane actuator 9.34 mm long and 25 μm thick (which is the thinnest Nafion membrane commercially available), the maximum peak tip displacement before back relaxation is 0.34 mm under 1.6 V as shown in figure 5(b) [19, 20]. Since the active layer thickness in ionomers is less than 2 μm [34], we assume the same t_c value (=1.5 μm) here to deduce the intrinsic strain S_{10}^i, which yields $S_{10}^i = 0.175\%$ for the Nafion membrane under 1.6 V. Although using different t_c will yield different S_{10}^i, the intrinsic strain in DPA-PS:BP is always much larger than that in Nafion films. The high strain plus a more than ten times higher elastic modulus, compared

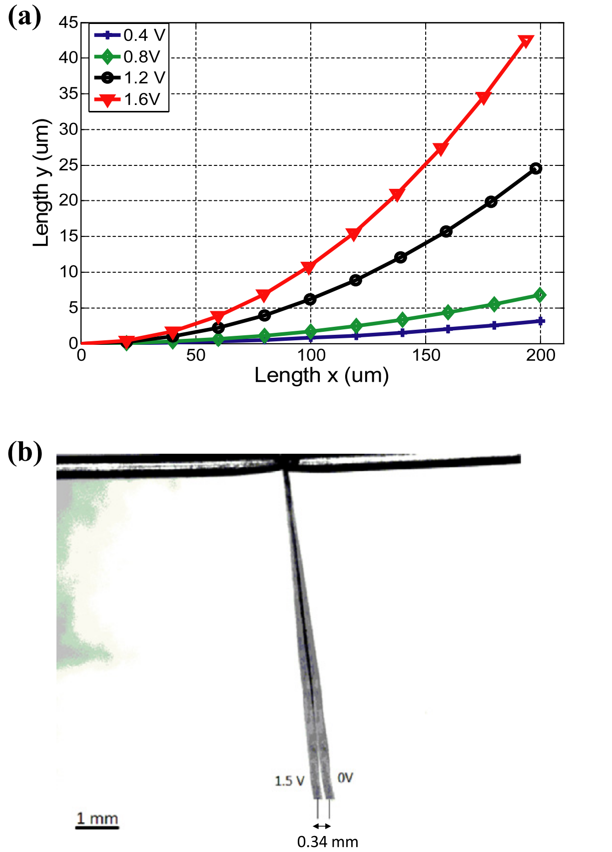

Figure 5. (a) The bending actuation profiles under different voltages measured by a Zygo profilometer. (b) The actuation data for Nafion^{TM} 211 (40 wt% BMI BF$_4$ uptake). The two images at 0 V and 1.6 V are merged to extract the tip deflection.

with Nafion, suggest DPA-PS:BS as a promising candidate ionomer matrix for i-EAP actuators.

4. Conclusions

This study demonstrates that DPA-PS:BP can be implemented as a new and promising ionomer for ionic polymer micro-actuators due to its high elastic modulus with high IL uptake and high electromechanical response. Compared with traditional ionomers employed in IPMCs which consist of a Teflon backbone and flexible side chains, DPA-PS:BP is composed of a highly aromatic and side-chain-free structure, which imparts this new class of ionomer with the ability to maintain a high elastic modulus at high electrolyte uptakes. The very slow decrease of the elastic modulus of DPA-PS:BP with IL uptake up to 50 vol% can be understood from the model in which the IL is distributed in the ionomer matrix as isolated spherical inclusions. The model is also utilized to explain the larger reduction in the elastic modulus beyond an IL uptake of 50 vol%, where the IL starts forming a fluid network within the ionomer. At 64 vol% of [BMIm][BF_4] uptake, the membrane displays a relatively high ionic conductivity $>4 \times 10^{-6}$ S cm^{-1} and a high elastic modulus of 600 MPa, which yields a large actuation of the ionomer actuator. Making use of the high elastic modulus and large strain response, a micro-actuator with membrane thickness down to 5 μm is fabricated using FIB and a tip displacement of 43 μm is generated under 1.6 V for an actuator of 200 μm long. In order to quantify the response, the intrinsic strain is deduced, which excludes the passive electrode layer effects. The intrinsic strain $>1.1\%$ with a considerable blocking stress of 180 kPa is obtained for a 200 μm long and 5 μm thick micro-actuator, which is much larger than that from the Nafion membrane actuators.

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